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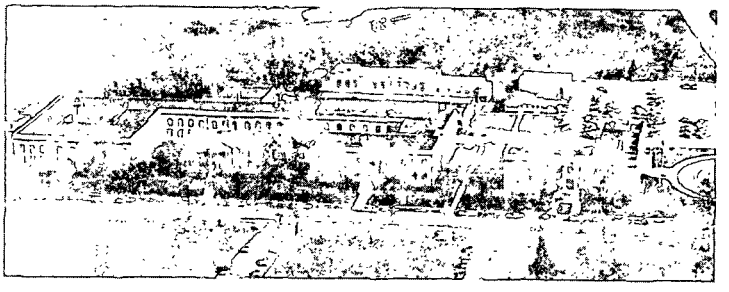

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DEGRADATION OF 1,5-ANHYDRORIBITOL AND 1,5-ANHYDROXYLITOL BY OXYGEN IN AQUEOUS SODIUM HYDROXIDE SOLUTIONS

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MAY, 1976

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INTRODUCTION

In recent years, environmental concerns have stirred interest in the use of oxygen and alkali for delignifying and brightening pulps. To take full advantage of these processes, the oxidative degradation of the wood polysaccharides has to be minimized. In the case of cellulose, degradation is manifested primarily as a decrease in viscosity caused by depolymerization. Additives, such as magnesium compounds, can decrease the degradation of carbohydrates to some extent and such ''stabilized'' processes have the advantage of greatly reducing effluent toxicity while producing pulps with acceptable papermaking properties. In order to increase the prospects for better control of carbohydrate degradation in oxygen-alkali, a workable knowledge of the reaction mechanism is necessary.

The present paper considers the basic questions of how the monomeric pyranoid ring is degraded by oxygen in an alkaline medium and whether the degradation is affected by the stereochemistry of the hydroxyl groups on the ring.

This paper has been submitted for publication in Carbohydrate Research.

DEGRADATION OF 1,5-ANHYDRORIBITOL AND 1,5-ANHYDROXYLITOL BY OXYGEN IN AQUEOUS SODIUM HYDROXIDE SOLUTIONS

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ABSTRACT

Degradations of both 1,5-anhydroribitol (1) and 1,5-anhydroxylitol (2) by oxygen in 1.25N sodium hydroxide at 120°C exhibited induction periods and produced hydrogen peroxide. The maximum concentration of hydrogen peroxide was attained at less than 10% reaction of 1 and 2. An organic peroxide intermediate was detected in reactions of 2, but not in reactions of 1. The rate of degradation of 1 was much greater than that of 2. The reaction of 1 was second order with respect to 1, while the reaction of 2 displayed complex kinetics indicative of autoinhibition by reactive intermediates. A free radical mechanism involving intermediate α-hydroxyhydroperoxidic species is proposed for the reactions of 1 and 2. In contrast to reactions of 1, the α-hydroxyhydroperoxidic species formed in reactions of 2 are postulated to be stabilized by intramolecular hydrogen bonding. The augmented stability of the α-hydroxyhydroperoxidic species would increase the importance of peroxy radical — peroxy radical termination reactions which produce nonradical products. The termination reactions, by decreasing the rate of the radical chain reaction, effect autoinhibition. The acidic degradation products formed from 1 and 2 were identical, but formed in different relative ratios. The major products were formic acid, acetic acid, lactic acid, glycolic acid, glyceric acid, 3-O-carboxymethyl-glyceric acid, and 1,4-anhydro-2-C-carboxy-tetritols. Possible pathways for formation of the products are presented.

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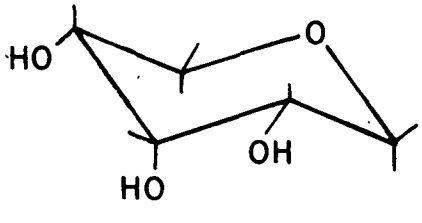
INTRODUCTION

During delignification of wood or pulp by molecular oxygen in alkaline media, degradation of the wood polysaccharides can be quite severe. The degradation is manifested primarily as a decrease in viscosity caused by depolymerization of the polysaccharides[1-3]. Studies of cellulosic model compounds[4-11] indicate that the depolymerization is caused by oxidation of hydroxyl groups of the monomeric glycose units to form carbonyl-containing intermediates which can undergo base-catalyzed β-elimination reactions to cleave the glycosidic linkages[12-14]. Oxidation is also postulated to produce α-dicarbonyl intermediates which on further oxidation yield dicarboxylic acids[8-9] or which can also undergo ring contraction *via* a benzilic acid-type rearrangement to form C-carboxy-furanoid species[8,9,11,15].

In this paper we report on a study of the degradation of 1,5-anhydroribitol (1) and 1,5-anhydroxylitol (2) by oxygen in aqueous sodium hydroxide. These model compounds were selected to determine whether the configuration of the hydroxyl groups of a pyranoid ring could affect the rate and mode of its degradation. Since the advent of this investigation, Malinen and Sjöström[11] have reported that methyl α-D-mannopyranoside degrades more rapidly than methyl α-D-glucopyranoside with oxygen in alkali, a fact which is consistent with the present results.



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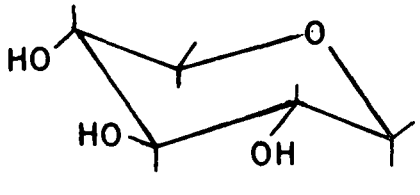


2

RESULTS

General — Degradations of 1 and 2 were studied using 1.25N NaOH, 120°C, 75 p.s.i. partial oxygen pressure (25°C), and both 0.01M and 0.1M anhydroalditol. Disappearance of the anhydroalditols was followed by quantitative g.l.c. analysis of deionized, acetylated samples of the reaction components.

The reactions exhibited short induction periods which were evident primarily when an initial anhydroalditol concentration of 0.01M was used and which were extremely variable in nature[16]. However, after the induction periods the reactions were very reproducible as illustrated in Figure 1.

Extreme variation in the rate of stirring of the reaction solutions had no effect on the rate of anhydroalditol degradation[16]. Thus, as has also been reported for alkali-oxygen reactions of other carbohydrates[17,18], diffusion of oxygen into the reaction solution must not be a rate-controlling factor in the degradations of 1 and 2.

1,5-Anhydroribitol (1) was degraded much more rapidly than 1,5-anhydroxylitol (2) (e.g., see Figure 1), a fact which must be attributed at least to the difference in the configuration of the hydroxyl group at C-3 of 1 and 2 and possibly to the configurational relationship between adjacent hydroxyl groups of 1 and 2. 1,5-Anhydroribitol has only cis 1,2-glycol groups while 1,5-anhydroxylitol has only trans 1,2-glycol groups. Similarly, methyl α-D-mannopyranoside is degraded more rapidly than its C-2 epimer, methyl α-D-glucopyranoside, with oxygen in aqueous NaOH[11].

Kinetic analysis — To determine the order of the reactions with respect to the anhydroalditol it was assumed that the oxygen and sodium hydroxide concentrations remained essentially constant during the reactions. Thus, the basic rate expression

given in equation (1) could be expressed as in equation (2) or equation (3).

$$-d[A]/dt = k[A]^a[O_2]^b[NaOH]^c \quad (1)$$

$$-d[A]/dt = k'[A]^a \quad (2)$$

$$\log (-d[A]/dt) = \log k' + a \log [A] \quad (3)$$

where A is 1 or 2; t is time; k is the rate constant; a, b, and c are the orders of the reaction with respect to the indicated reactant; and $k' = k[O_2]^b[NaOH]^c$ and is essentially constant.

The solubility of oxygen in the reaction solution would be low, ca. 2.5×10^{-3}M[19], and hence, it would not be present in large excess relative to the anhydroalditol. However, since diffusion of oxygen into the reaction solution was not a rate-determining factor, the constant oxygen pressure maintained over the reaction solution insured that the concentration of oxygen was constant throughout the reactions.

For reactions with 0.01M anhydroalditol, the sodium hydroxide concentration (1.25N) was in large excess relative to that of 1 or 2 and thus its concentration remained essentially constant throughout the reactions. For 0.1M anhydroalditol the assumption that the sodium hydroxide concentration remains essentially constant in the reaction would at first seem to be inappropriate, particularly for reactions of 1 which were analyzed to 80-90% completion. However, kinetic analyses of reactions of 1 using this assumption indicated a second-order dependence on 1 at both 0.01M and 0.1M 1. This would not be expected if the sodium hydroxide concentration decreased enough over the period of analysis to drastically affect the rate of reaction.

The reactions were analyzed by the differential method using equation (3)[20]. The variable induction periods made utilization of the differential method involving

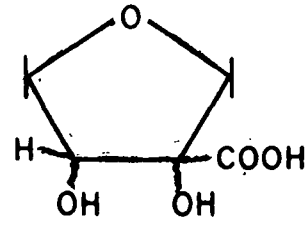
variation of initial reaction conditions impractical. However, since the degradation rate attained after the induction period was essentially the same for duplicate experiments (see Figure 1), the differential method employing single kinetic trials was applicable. Analysis entailed measuring the reaction rate at various reaction times corresponding to a number of reactant concentrations and plotting the data according to equation (3) as illustrated in Figure 2. The slope of the line is a, the order of the reaction with respect to the anhydroalditol. Values of a obtained for reactions of 1,5-anhydroribitol (1) were 2.08 and 2.02 at 0.01M and 0.1M 1, respectively. In contrast the a values for reactions of 1,5-anhydroxylitol (2) were 3.03 and 3.46 at 0.01M and 0.1M 2, respectively. The value of a for reactions of 2 also increased at early reaction times corresponding to higher concentrations of 2 (see Figure 2).

Products — (a) Peroxides. The concentrations of hydrogen peroxide and organic peroxides formed in reactions of 1 and 2 were determined by a modified colorimetric method[16,21-23]. The procedure is based on the fact that hydrogen peroxide will complex with titanium(IV). Hydrogen peroxide which complexes rapidly with the reagent can be differentiated from organic peroxides which must first hydrolyze to form hydrogen peroxide by measuring the change in the absorbance in the sample with time. The estimate of the organic peroxide concentration is probably low since the extent of their hydrolysis is not known and organic peroxides may undergo decomposition reactions other than hydrolysis.

As illustrated in Figure 3A, hydrogen peroxide was formed in reactions of both 1 and 2. The maximum concentration of hydrogen peroxide was attained at approximately 10% reaction of the anhydroalditol for both reactions, but the maximum concentration of hydrogen peroxide in the reaction of 1 was greater than twice that in the reaction of 2.

The organic peroxide profile for reactions of 1 and 2 were drastically different (see Figure 3B). No organic peroxides were detectable in the reactions of 1 at early reaction times. At longer reaction times some organic peroxides were detected but the results are inconclusive. In sharp contrast, the organic peroxide concentration exhibited a maximum early in the reaction of 2, decreased to a minimum, and then increased. Thus, an organic peroxide intermediate is formed, in significant concentration, early in the degradation of 2.

(b) Carboxylic acids. The acidic products formed in the degradations of 1 and 2 were the same. The major products were formic acid (3), acetic acid (4), lactic acid (5), glycolic acid (6), glyceric acid (7), 2,3-dihydroxybutyric acid (8), 3-O-carboxymethylglyceric acid (9), and an isomeric mixture of 1,4-anhydro-2-C-carboxy-tetritols (10). 3-Hydroxypropanoic acid (11), 2-hydroxybutyric acid (12), and 2,4-dihydroxybutyric acid (13) were minor degradation products. Potential pathways for formation of these products are presented later in Figure 6.



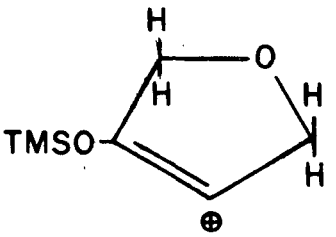
10

Formic acid and acetic acid were identified as their benzyl esters by comparison of their g.l.c. retention times with authentic materials.

Lactic acid, glycolic acid, and glyceric acid in combination with 2,3-dihydroxybutyric acid[24] were identified as their per-O-trimethylsilyl (TMS) derivatives by comparison of their g.l.c. retention times and g.l.c.-m.s. spectra with those of authentic materials. 3-O-Carboxymethylglyceric acid, 3-hydroxypropanoic acid,

2-hydroxybutyric acid, and 2,4-dihydroxybutyric acid were identified as their TMS derivatives by g.l.c.-m.s. Analysis of the mass spectra of the acids relied heavily on the studies of Petersson[25,26].

The isomeric 1,4-anhydro-2-C-carboxy-tetritols (10), analogous to the methyl C-carboxy-furanosides formed in similar reactions of methyl glycosides[8,9,11], were identified as their TMS derivatives by g.l.c.-m.s. The major diagnostic peaks were m/e 364 (P+), 349 (P+-15), and 157.

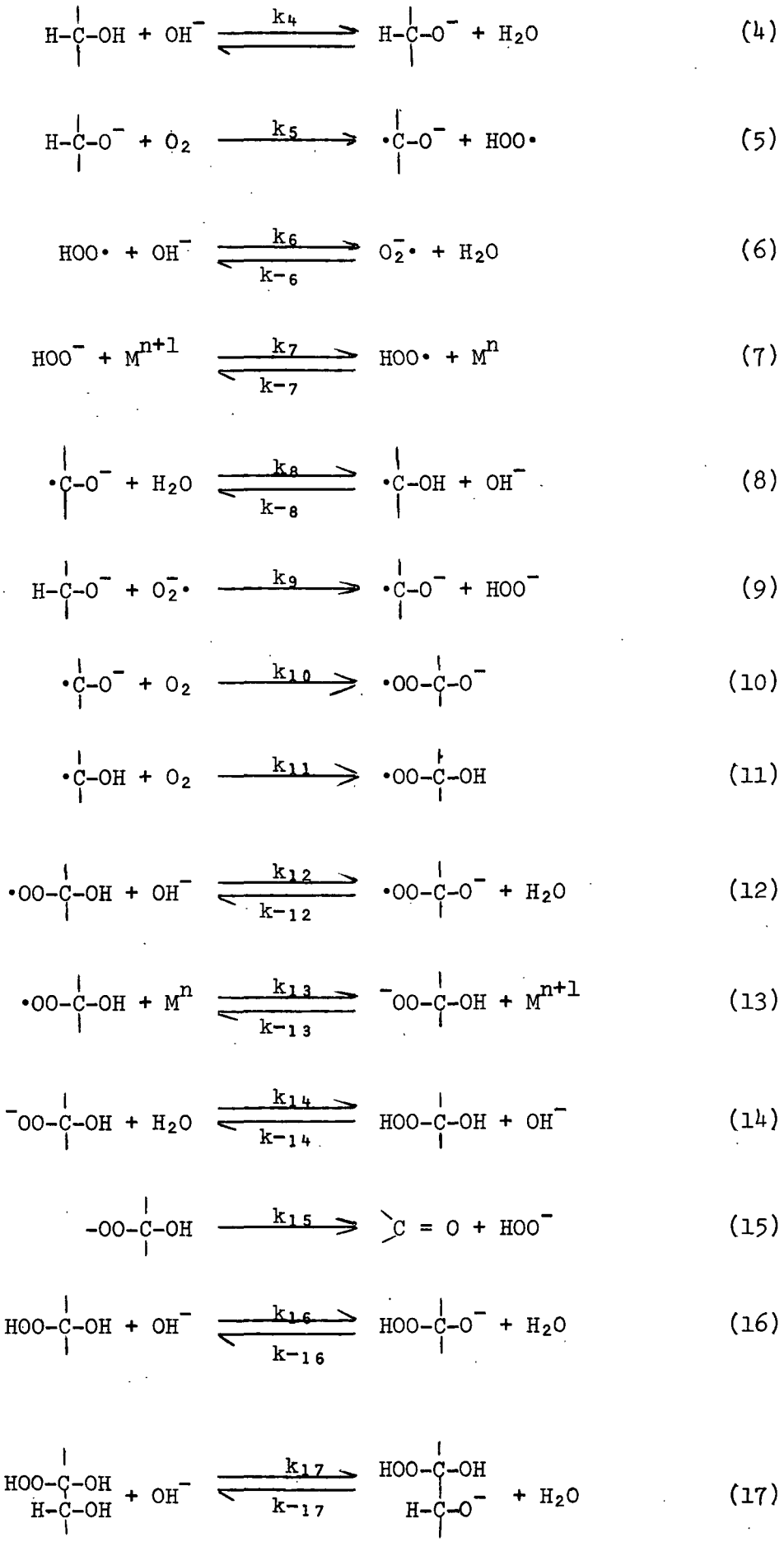


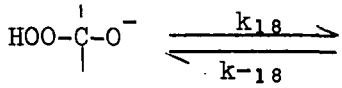
m/e 157

Quantitative analyses of the major products, excluding acetic and formic acid, as a function of the extent of reaction of 1 and 2 are shown in Figure 4. Lactic acid and glycolic acid are fairly stable products, as indicated by the fact that their rate of formation was at all times equal to or greater than their rate of degradation. In contrast, glyceric acid, 2,3-dihydroxybutyric acid, and the anhydrotetritols (10), all of which contain 1,2-glycol groups, degrade in the reaction systems. It is uncertain whether 3-O-carboxymethylglyceric acid is stable in the reaction media.

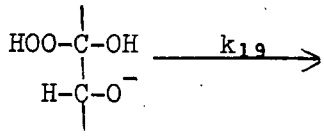
DISCUSSION

A mechanism proposed for the degradation of 1 and 2 by oxygen in alkaline media is given in equations (4) through (22). The mechanism, based on both the present results and several studies of other investigators, can account for the observed induction periods, the formation of hydrogen peroxide and an organic peroxide intermediate, the kinetics of the reactions, and the formation of acidic degradation products.


H-C-OH + OH⁻ ⇌ (k4, k-4) H-C-O⁻ + H2O (4)
H-C-O⁻ + O2 → (k5) ·C-O⁻ + HOO· (5)
HOO· + OH⁻ ⇌ (k6, k-6) O2⁻· + H2O (6)
HOO⁻ + M^n+1 ⇌ (k7, k-7) HOO· + M^n (7)
·C-O⁻ + H2O ⇌ (k8, k-8) ·C-OH + OH⁻ (8)
H-C-O⁻ + O2⁻· → (k9) ·C-O⁻ + HOO⁻ (9)
·C-O⁻ + O2 → (k10) ·OO-C-O⁻ (10)
·C-OH + O2 → (k11) ·OO-C-OH (11)
·OO-C-OH + OH⁻ ⇌ (k12, k-12) ·OO-C-O⁻ + H2O (12)
·OO-C-OH + M^n ⇌ (k13, k-13) ⁻OO-C-OH + M^n+1 (13)
⁻OO-C-OH + H2O ⇌ (k14, k-14) HOO-C-OH + OH⁻ (14)
-OO-C-OH → (k15) >C = O + HOO⁻ (15)
HOO-C-OH + OH⁻ ⇌ (k16, k-16) HOO-C-O⁻ + H2O (16)
HOO-C-OH / H-C-OH + OH⁻ ⇌ (k17, k-17) HOO-C-OH / H-C-O⁻ + H2O (17)



(18)



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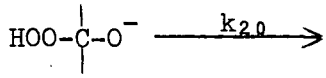
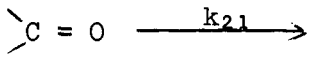


(20)



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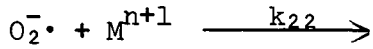
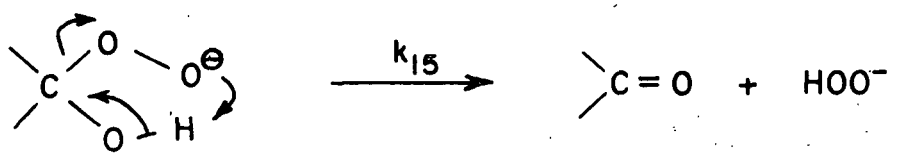


(22)

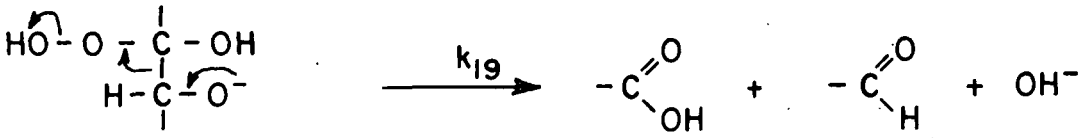
where H-C-OH is a carbinol group of either 1 or 2 and M is a catalytic metal.

Analogous with other reactions of carbohydrates with oxygen in alkaline media[6,7,10,27], the degradations of 1 and 2 exhibited induction periods during which the hydrogen peroxide concentration increased. The initial step of the oxidative degradation is believed to be ionization of a hydroxyl group [reaction (4)][6,7,10,11]. Formation of the oxyanion facilitates abstraction of the geminal hydrogen atom by oxygen to form the hydroperoxy radical (HOO•) and the ketyl radical [reaction (5)]. The hydroperoxy radical would exist primarily as its conjugate base, the superoxide radical (O_2^-•), in the alkaline system [reaction (6)][28]. When the superoxide radical concentration reaches the threshold level, rapid degradation of the anhydroalditols (1 and 2) is believed to be propagated by a free radical chain reaction involving an α-hydroxyhydroperoxide intermediate [reactions (6) through (18)]. The α-hydroxyhydroperoxide would be formed by reaction of oxygen with either the ketyl radical or its conjugate acid [reactions (10) and (11)] and a subsequent one-electron transfer involving a catalytic metal ion [reaction (13)][29]. Carbonyl groups can be formed from either conjugate base of the α-hydroxyhydroperoxide [reactions (15) and (18)]. Reaction (15) is believed to occur by a cyclic process as indicated in equation (15a). The acidic products



(15a)

can be formed from intermediates containing carbonyl groups [reaction (21)][4,5,7-15] or directly from an intermediate containing an ionized α-hydroxyhydroperoxy group [reactions (19) and (20)], as proposed by Isbell[30] and as indicated in equations (19a) and (20a).



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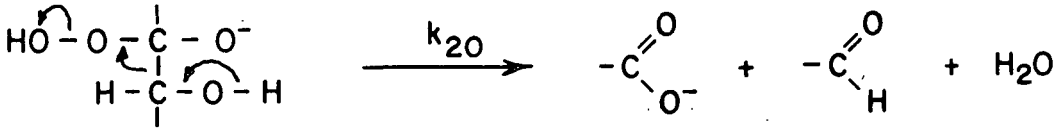


(20a)

Termination of the radical chain reaction can be effected by the reverse of reaction (7) and reaction (22).

A rate of expression for the disappearance of the anhydroalditols, A, was derived on the basis of the proposed reaction mechanism by making steady-state approximations for the radical species and the catalytic metal ions[16].

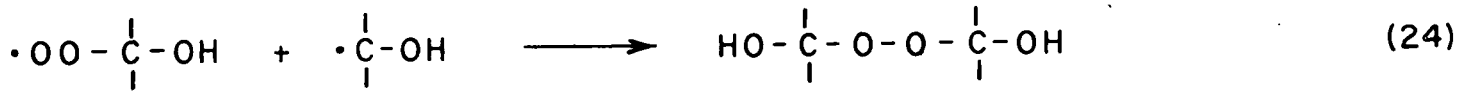
$$-d[A]/dt = K_4 k_5 [A][OH^-][O_2] + K_4^2 k_5 k_9 [A]^2[OH^-]^2[O_2]/k_{22}[M^{n+1}] \quad (23)$$

The first term of the rate expression describes the induction period which would exhibit a first-order dependence on the anhydroalditol, sodium hydroxide, and oxygen. The metal ion concentration in the denominator of the second term, being very small, makes this term large relative to the first term. Thus, equation (23) indicates that, after the induction period, the reactions of 1 and 2 should exhibit a second-order dependence on the anhydroalditol. This was found to be the case for 1,5-anhydroribitol (1), but 1,5-anhydroxylitol (2) exhibited higher orders of reaction (see Figure 2). A potential explanation for the difference between 1 and 2 is given later.

Based on equation (23), the reactions of the anhydroalditols would be expected to exhibit a second-order dependence on the sodium hydroxide concentration also. This was not tested experimentally. Previously it was reported that the reaction of methyl β-D-glucopyranoside with oxygen in aqueous sodium hydroxide exhibited approximately a first-order dependence on the alkali concentration[7,10]. However, there are indications that the order of the methyl β-D-glucopyranoside reaction with respect to the hydroxide concentration may be variable, attaining a higher order as the alkali concentration is increased[31].

When the hydroxyl radical (HO•) was also considered to be a reactive species in the anhydroalditol degradations, a rate expression similar to equation (23), but including a third term indicative of the role of the hydroxyl radical was generated[16]. The additional term has a first-order dependence on the anhydroalditol. Since the degradation of 1 was found to be second order with respect to 1, it can be inferred that the hydroxyl radical does not play a major role in the reaction. This is consistent with the supposition that the hydroxyl radical would not be an important chain propagating radical in oxidations in which the metal ion concentration is extremely small[32].

Reactions of 1,5-anhydroxylitol (2) exhibited higher reaction orders with respect to the alditol than reactions of 1,5-anhydroribitol (1). This is attributed to autoinhibition of reactions of 2 by a reactive intermediate which would make the reaction order in 2 as a function of time, as determined, greater than the order in 2 with respect to the initial concentration or true order[20]. The inhibitor is postulated to be a species containing a stabilized α-hydroxy-hydroperoxy free radical. The mechanisms of degradation of 1 and 2 are considered to be the same except that radical chain termination by reactions (24) and (25)* which involve α-hydroxyhydroperoxy radicals are proposed to play a major role in reactions of 2. Because these reactions produce only nonradical products, they would cause the radical chain reaction to slow down and thereby retard the rate of degradation of 2.



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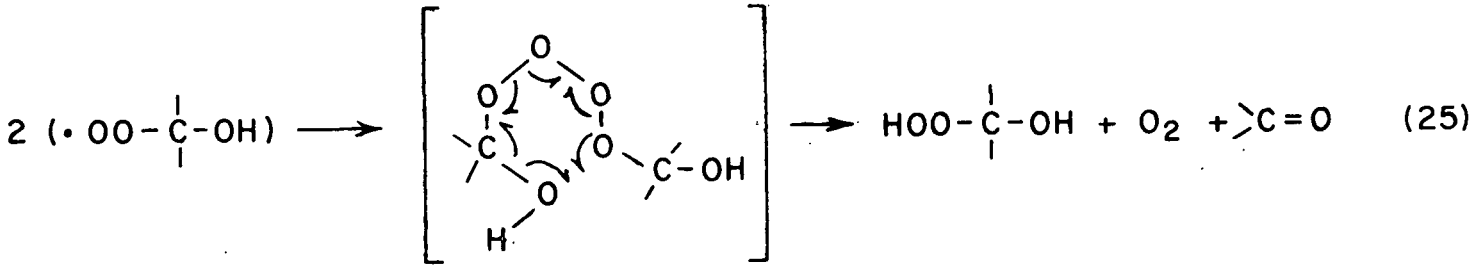
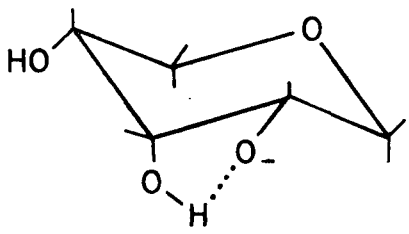


(25)

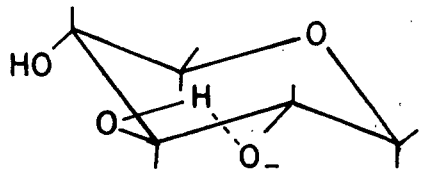
*Reaction (25) is proposed to occur through the decomposition of a tetroxide intermediate via a cyclic transition state[33]. Tetroxides derived from tertiary peroxy radicals have been shown to be quasi-stable species at low temperature[34].

In order for reactions (24) and (25) to be important in reactions of 2 and not in reactions of 1, the concentration of species containing α-hydroxyhydroperoxy radicals must be substantially greater in reactions of 2 than in reactions of 1. The reaction of 1 produced essentially no detectable organic peroxides while the concentration of organic peroxides in the reaction of 2 exhibited a maximum early in the reaction, decreased to a minimum, and subsequently increased (see Figure 3). The organic peroxide curve for the reaction of 2 can be rationalized as a build up and subsequent degradation of α-hydroxyhydroperoxides in conjunction with a slower build up of dialkyl peroxides. A potential explanation for the difference in the concentration of α-hydroxyhydroperoxidic species in reactions of 1 and 2 is given in the ensuing discussion.

Equatorial hydroxyl groups of 1 and 2 should ionize preferentially since the resulting oxyanions, being less hindered than their axial counterparts, are more easily solvated[35]. The anions, A^-, would also be stabilized by hydrogen bonding with the hydroxyl group on the adjacent carbon atom[36]. Thus, for 1, ionization of OH-2 or OH-4 would occur preferentially with the molecule in the C_1^4 conformation



A^- (1)



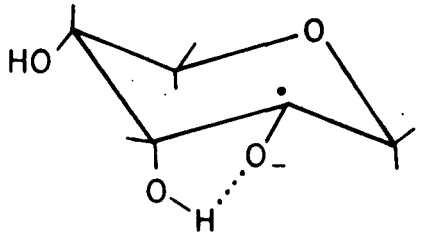
A^- (2)

while ionization at OH-3 would be preferred in the C_4^1 conformation*. For 2, all of the hydroxyl groups are equatorial in the C_1^4 conformation. For simplicity only

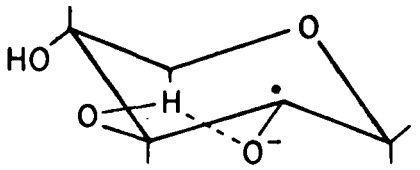
*The ratios of the C_1^4 to the C_4^1 conformer for 1 and 2 in water at 25°C have been estimated to be 74:26 and 95:5, respectively[37].

reactions initiated by ionization of OH-2 of 1 and 2 in the C_1^4 conformation will be discussed. However, the same stereochemical implications apply to any of the equatorial hydroxy groups of 1 or 2.

The next step in the radical chain reaction is abstraction of the hydrogen atom geminal to the oxyanion by the superoxide radical to form the ketyl radical, $\underline{A}^{\cdot}$ [reaction (9)]. Abstraction of the hydrogen atom is facilitated by the increased

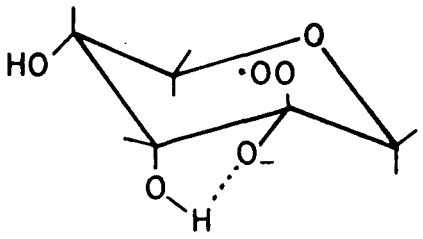


$A^{\cdot}$ (1)

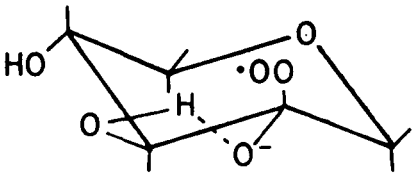


$A^{\cdot}$ (2)

electron density provided by the oxyanion. The hydrogen bonding and solvation effects would help stabilize the ketyl radical, $\underline{A}^{\cdot}$, toward inversion, particularly in $\underline{A}^{\cdot}$(1). Thus, subsequent reaction of $\underline{A}^{\cdot}$ with oxygen [reaction (10)] would selectively form the conjugate base of the α-hydroxyhydroperoxy radical ($^{-}\underline{AO_2}\cdot$) in which the configuration of the hydroxyl groups of $\underline{A}^{\cdot}$ is retained. In addition,



$^{-}AO_2^{\cdot}$ (1)



$^{-}AO_2^{\cdot}$ (2)

reaction (10) would be expected to have essentially a zero activation energy[38-40]. Thus, once $\underline{A}^{\cdot}$ is formed it would react very rapidly with oxygen in its vicinity. This would also aid in making reaction (10) stereoselective.

A species containing an α-hydroxyhydroperoxy radical ($\underline{AO_2^{\bullet}}$) or an α-hydroxyhydroperoxy anion ($\underline{AO_2^-}$) is subsequently formed from -$\underline{AO_2^{\bullet}}$ [reactions (12) and (13)]. Unlike its counterpart in the reaction of 1, the $\underline{AO_2^-}$ produced in the reaction of 2 can form an effective intramolecular hydrogen bond between the peroxyanion and the hydroxyl group on the adjacent carbon atom. The pertinent minimum oxygen-oxygen distances for $\underline{AO_2^-}$ of 1 and 2 are 3.7 Å and 2.1 Å, respectively, as shown in Figure 5. These oxygen-oxygen distances would be the same, respectively, for any α-hydroxyhydroperoxy anion formed at a carbon atom having an equatorial hydroxy group in 1 and 2. In solution, the oxygen-oxygen distance is critical in determining the strength of a hydrogen bond. Based on neutron diffraction studies on ice[41], the optimum oxygen-oxygen distance for hydrogen bonding is approximately 2.8 Å. Oxygen atoms that can theoretically approach each other at distances less than 2.8 Å can also move apart to attain the optimum distance for hydrogen bonding. Thus, only α-hydroxyhydroperoxy anions formed from 1,5-anhydroxylitol (2) are capable of being stabilized through effective hydrogen bonding.

It is also probable that α-hydroxyhydroperoxy radicals ($\underline{AO_2^{\bullet}}$) formed from (2), but not those from (1), can hydrogen bond with hydroxyl groups on adjacent carbon atoms in a manner similar to the anions ($\underline{AO_2^-}$). Rust and Youngman[42], in a study of autoxidation of pentanediols, concluded that intramolecular hydrogen bonding enhances a peroxy radical's stability and hence increases the importance of self-termination reactions.

Thus, intramolecular hydrogen bonding can increase the stability of both the α-hydroxyhydroperoxy radical ($\underline{AO_2^{\bullet}}$) and the α-hydroxyhydroperoxy anion ($\underline{AO_2^-}$) which are formed in reactions of 2 and hence increase their concentrations in the system. In addition, hydrogen bonding in $\underline{AO_2^-}$ would decrease product formation by ionic pathways such as reactions (15a), (18), and (20a). Therefore, since $\underline{AO_2^-}$ and $\underline{AO_2^{\bullet}}$ are interconvertible [reaction (13)], the net result is that the $\underline{AO_2^{\bullet}}$

concentration is effectively increased to the point where the bimolecular radical termination reaction [reaction (25)] becomes important and effects autoinhibition of the degradation of 2.

Based on the preceding discussion, the inhibiting effects of $AO_2^{\bullet}$ should increase as its concentration increases. It is evident from Figure 3 that the concentration of hydroperoxidic species is greatest early in the reaction of 2. Figure 2 shows that the apparent reaction order with respect to 2 increases at early reaction times corresponding to the highest concentration of hydroperoxides.

Potential reaction pathways for formation of the acidic products identified in reactions of 1 and 2 are illustrated in Figure 6. Once a carbonyl group is introduced into the alditol ring, rapid alkaline rearrangements can shift the carbonyl moiety to any carbon atom containing a hydroxyl group. The ring can then be opened by elimination reactions and the resultant acyclic dicarbonyl intermediates can form the carboxylic acids[43-45]. In addition, products such as lactic acid (5) and glycolic acid (6) must also be formed from other products (see Figure 4). Before ring cleavage occurs, a second carbonyl group can be introduced adjacent to the first one. The α-dicarbonyl intermediate can undergo carbon-carbon bond cleavage to form dibasic acids (9) or undergo a benzylic acid-type rearrangement to produce the 1,4-anhydro-2-C-carboxy-tetritols (10)[8,9,15].

EXPERIMENTAL

Analytical methods. — Melting points were determined on a Thomas-Hoover capillary apparatus which was calibrated against known compounds. Optical rotations were determined on a Perkin-Elmer 141 MC polarimeter. Colorimetric analyses were performed on a Beckman DU spectrophotometer. Atomic absorption spectra were determined on a Perkin-Elmer 305 instrument.

G.l.c. analyses were performed on a Varian Aerograph 1200 instrument equipped with a hydrogen flame ionization detector and a Honeywell Electronic 16 recorder with a Disc integrator. The columns were housed in 0.125 in stainless steel tubing and were arranged for on-column injection. The following columns and operating conditions were employed: (A) 10% SE-30 on 60-80 mesh DMCS-AW Chromosorb W (5 ft); N_2, 15 ml min^{-1}; column, 165°; injector, 260°; and detector 260°; (B) 10% SE-30 on 60-80 mesh DMCS-AW Chromosorb W (5 ft); N_2, 8 ml min^{-1}; column, 185°; injector, 260°; and detector, 260°; (C) 3% OV-17 on 80-100 mesh Supelcoport (10 ft); N_2, 30 ml min^{-1}; column, 120°; injector, 160°; and detector, 190°; and (D) 3% OV-17 on 80-100 mesh Supelcoport (10 ft); N_2, 15 ml min^{-1}; column, 70° for 22 min then programmed at 4° min^{-1} for 17 min and subsequently 1° min^{-1} to completion; injector, 265°; and detector, 265°.

Mass spectra were determined on a Du Pont Instruments 21-491 spectrometer interfaced with a Varian Aerograph 1440 gas chromatograph. G.l.c. conditions D using helium as the carrier gas were used.

1,5-Anhydroribitol (1). — 2,3,4-Tri-O-benzoyl-β-D-ribopyranosyl bromide[46] was hydrogenated in the presence of 10% palladium on carbon[47]. The product mixture was debenzoylated with sodium methoxide in methanol-chloroform (20:1, vol), refluxed with 0.1N NaOH for 2 h, deionized with Amberlite MB-3 resin, decolorized, and isolated as a clear sirup. Crystallization from the sirup in ethanol-ethyl acetate (1:1, vol) yielded 1 (80% yield); m.p. 128-129°, $[\alpha]_D$ 0° (H_2O). [Lit.[46] m.p. 128-129°, $[\alpha]_D$ 0° (H_2O)].

1,5-Anhydroxylitol (2). — Phenyl 2,3,4-tri-O-acetyl-1-thio-β-D-xylopyranoside[48] was reduced with W-2 Raney nickel in ethanol[49]. The product mixture was deacetylated with sodium methoxide in methanol, treated with 0.1N NaOH, deionized with Amberlite MB-3 resin, decolorized and isolated as a sirup. Crystallization from the sirup in absolute ethanol yielded 2 (77% yield); m.p. 115-116°, $[\alpha]_D$ 0° (H_2O). [Lit.[49] m.p. 116-117°, $[\alpha]_D$ 0° (H_2O)].

Kinetic analyses. — Sodium hydroxide solutions for kinetic experiments were freshly prepared from a carbonate-free 50% (wt) NaOH stock solution by diluting the stock solution with carbon dioxide-free, triply-distilled water under a nitrogen atmosphere[16].

The reactor system, described in detail elsewhere[16], consisted of a 250 ml capacity teflon-lined brass reactor which could be sampled while hot and under pressure, and an oil bath assembly which could control the reactor temperature at 120 ± 0.2°.

The reactor was loaded and assembled in a nitrogen atmosphere, connected to the sampling system and the oil bath apparatus, lowered into the heated oil bath, and allowed to thermally equilibrate. A zero-time sample was then taken and the reaction was initiated by pressurizing the reactor to a partial oxygen pressure of 75 p.s.i. (25°). The size of the samples and the amount of internal standard solution added to the samples were determined gravimetrically. 1,6-Anhydro-β-D-glucopyranose and methyl β-D-xylopyranoside were used as the internal standards for reactions of 1 and 2, respectively.

Samples (ca. 1.5 ml) of the reaction solution containing the internal standard were deionized on an Amberlite MB-3 (H^+,OH^-) column (6-8 ml), concentrated in vacuo to dryness, and acetylated with acetic anhydride (0.25 ml) in pyridine (0.75 ml) for 18 h. The acetylation mixtures were diluted with distilled water, shaken for 0.5 h, and extracted with chloroform (2 x 5 ml). The chloroform extracts were washed with N HCl (15 ml) and water (10 ml), dried (Na_2SO_4), and concentrated in vacuo to dryness. The dried samples were dissolved in chloroform (ca. 0.2 ml) and analyzed by g.l.c. using conditions B for reactions of 1 and conditions A for reactions of 2.

Product analyses. — Peroxide analyses were performed in conjunction with all kinetic experiments using 0.1N carbohydrate. The peroxide concentrations were

determined by a modification of the colorimetric method using titanium sulfate reagent[16,23]. A sample of the reaction solution (1.0 ml) was neutralized with 0.5N H_2SO_4 to ca. pH 6-7, treated with titanium sulfate reagent (0.2 ml), and diluted to volume (10.0 ml) with water. At that point the solution had ca. pH 1. The hydrogen peroxide concentration was estimated from the initial absorbance (420 nm) of the solution. The organic peroxide concentration was estimated from the maximum increase in the absorbance over the succeeding 36 h. The procedure was calibrated using hydrogen peroxide solutions of known concentration. A sample of the reactions which were monitored for peroxides was also analyzed for cadmium, cobalt, copper, chromium, iron, magnesium, manganese, nickel, and zinc by atomic absorption.

Formic and acetic acid were identified as reaction products as their benzyl esters[50] by comparison of their g.l.c. retention times (T_r) with authentic materials. A sample (ca. 3.0 ml) of the reaction solution was eluted through an Amberlite IR-120 (H^+) resin column (5 ml) with distilled water (15 ml). The eluate was titrated to ca. pH 8 with 0.03M tetra-n-butyl ammonium hydroxide and concentrated in vacuo to a sirup. The sirup was dissolved in anhydrous acetone (3 ml) and allowed to react with benzyl bromide (0.5 ml) for 2 h. The acetone solution was analyzed directly by g.l.c. using conditions C.

The other acidic reaction products were analyzed as their per-O-trimethylsilyl derivatives by g.l.c. The products were identified by comparison of their retention times with that of authentic materials when possible, and by g.l.c.-M.S. analysis[16]. A sample (ca. 3.0 ml) of the reaction solution was eluted through an Amberlite IR-120 (H^+) resin column (5 ml) with distilled water (15 ml). The eluate was concentrated in vacuo to a sirup. The sirup was dried by adding 1,2-dichloroethane and concentrating the mixture in vacuo. The sirup was dissolved in dimethylsulfoxide (0.3 ml) and Tri-Sil Concentrate (0.5 ml) was added to the

solution. The mixture was shaken for 24 h and then the top layer of the two phase system was analyzed by g.l.c. using conditions D. For semiquantitative analysis of the products a solution of internal standard, methyl β-D-xylopyranoside, was added to the sample of the reaction solution prior to the ion exchange procedure. Response factors were determined for lactic, glycolic, and glyceric acids by subjecting them to the analytical procedure. The response factors used for the 1,4-anhydro-2-C-carboxy-tetritols and 3-O-carboxymethylglyceric acid were estimates based on their molecular weights.

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REFERENCES

1 A. Robert, P. Rérolle, A. Viallet, and O. Martin-Borret, A.T.I.P. Bull., 18 (1964) 151-176.

2 A. Robert and A. Viallet, A.T.I.P. Rev., 25 (1971) 237-241.

3 G. L. Akim and A. Ya. Frank, Cellulose Chem. Technol., 7 (1973) 441-450, and references cited therein.

4 R. D. Brooks and N. S. Thompson, Tappi, 49 (1966) 362-366.

5 O. Samuelson, Das Papier, 24 (1970) 671-678.

6 J. L. Minor and N. Sanyer, J. Polymer Sci. C, 36 (1971) 73-84.

7 J. D. Sinkey and N. S. Thompson, Paperi Puu, 56 (1974) 473-486.

8 B. Ericsson, B. O. Lindgren, and O. Theander, Cellulose Chem. Technol., 8 (1974) 363-385; B. Ericsson, B. O. Lindgren, O. Theander, and G. Petersson, Carbohyd. Res., 23 (1972) 323-325.

9 B. Ericsson and R. Malinen, Cellulose Chem. Technol., 8 (1974) 327-338.

10 J. T. McCloskey, L. R. Schroeder, J. D. Sinkey, and N. S. Thompson, Paperi Puu, 57 (1975) 131-145.

11 R. Malinen and E. Sjöström, Cellulose Chem. Technol., 9 (1975) 231-238.

12 J. F. Haskins and M. J. Hogsed, J. Org. Chem., 15 (1950) 1264-1274.

13 A. Meller, Holzforschung, 14 (1960) 129-139.

14 O. Theander, Tappi, 48 (1965) 105-110.

15 R. Malinen, Paperi Puu, 57 (1975) 193-204.

16 E. C. Millard, Doctoral Dissertation, The Institute of Paper Chemistry, Appleton, Wis., June, 1976.

17 W. B. Gleason and R. Barker, Can. J. Chem., 49 (1971) 1425-1432.

18 H. G. J. Dewilt and B. F. M. Kuster, Carbohyd. Res., 19 (1971) 5-15.

19 G. Bruhn, J. Gerlach, and F. Pawlek, Z. Anorg. Chem., 337 (1965) 68-79.

20 K. J. Laidler, Reaction Kinetics, Vol. 1, MacMillan, New York, 1963.

21 C. N. Satterfield and A. H. Bonnell, Anal. Chem., 27 (1955) 1174-1175.

22 H. Probiner, Anal. Chem., 33 (1961) 1423-1426.

23 S. Marklund, Acta Chem. Scand., 25 (1971) 3517-3531.

24 F. W. Bachelor and G. A. Miana, Can. J. Chem., 47 (1969) 4089-4091.

25 G. Petersson, Tetrahedron, 26 (1970) 3413-3428.

26 G. Petersson, Org. Mass Spectrom., 6 (1972) 577-592.

27 O. Samuelson and L. Stolpe, Svensk Papperstidn., 72 (1969) 662-666.

28 D. Behar, G. Czapski, J. Robini, L. M. Dorman, and H. A. Schwarz, J. Phys. Chem., 74 (1970) 3209-3213.

29 C. Walling and A. Goosen, J. Amer. Chem. Soc., 95 (1973) 2987-2991.

30 H. S. Isbell, Adv. Chem. Ser., 117 (1973) 70-87.

31 J. T. McCloskey, Doctoral Dissertation, The Institute of Paper Chemistry, Applton, Wis., January, 1971.

32 C. Walling, Free Radicals in Solution, John Wiley and Sons, New York, 1957, p. 427-430, 565-575.

33 G. A. Russel, J. Amer. Chem. Soc., 79 (1957) 3871-3877.

34 R. Hiatt, in Organic Peroxides, Vol. II, D. Swern (Ed.), Wiley-Interscience, New York, 1971, p. 88.

35 E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, Conformational Analysis, Interscience, New York, 1965, p. 274.

36 J. A. Rendleman, Jr., Adv. Chem. Ser., 117 (1973) 51-69.

37 L. J. Pitzner and R. H. Atalla, Spectrochim. Acta, 31A (1975) 911-929.

38 K. U. Ingold, Chem. Rev., 61 (1961) 563-589.

39 G. A. Russel, A. G. Bemis, E. J. Geels, E. G. Janzen, and A. J. Moye, Adv. Chem. Ser., 75 (1968) 174-201.

40 A. Fish, in Organic Peroxides, Vol. I, D. Swern (Ed.), Wiley-Interscience, New York, 1970, p. 143.

41 S. W. Peterson and H. A. Levy, Acta Cryst., 10 (1957) 70-79.

42 F. F. Rust and E. A. Youngman, J. Org. Chem., 27 (1962) 3778-3781.

43 B. Lindberg and O. Theander, Acta Chem. Scand., 22 (1968) 1782-1786.

44 B. Ericsson, B. O. Lindgren, and O. Theander, Cellulose Chem. Technol., 7 (1973) 581-591.

45 R. Malinen and E. Sjöström, Paperi Puu, 54 (1972) 451-468.

46 R. W. Jeanloz, H. G. Fletcher, Jr., and C. S. Hudson, J. Amer. Chem. Soc., 70 (1948) 4052-4054.

47 S. Jacobsen and C. Pedersen, Acta Chem. Scand., 27 (1973) 3111-3117.

48 C. B. Purves, J. Amer. Chem. Soc., 51 (1929) 3619-3627.

49 H. G. Fletcher, Jr. and C. S. Hudson, J. Amer. Chem. Soc., 69 (1947) 921-924.

50 P. O. Bethge and K. Lindström, Analyst, 99 (1974) 137-142.

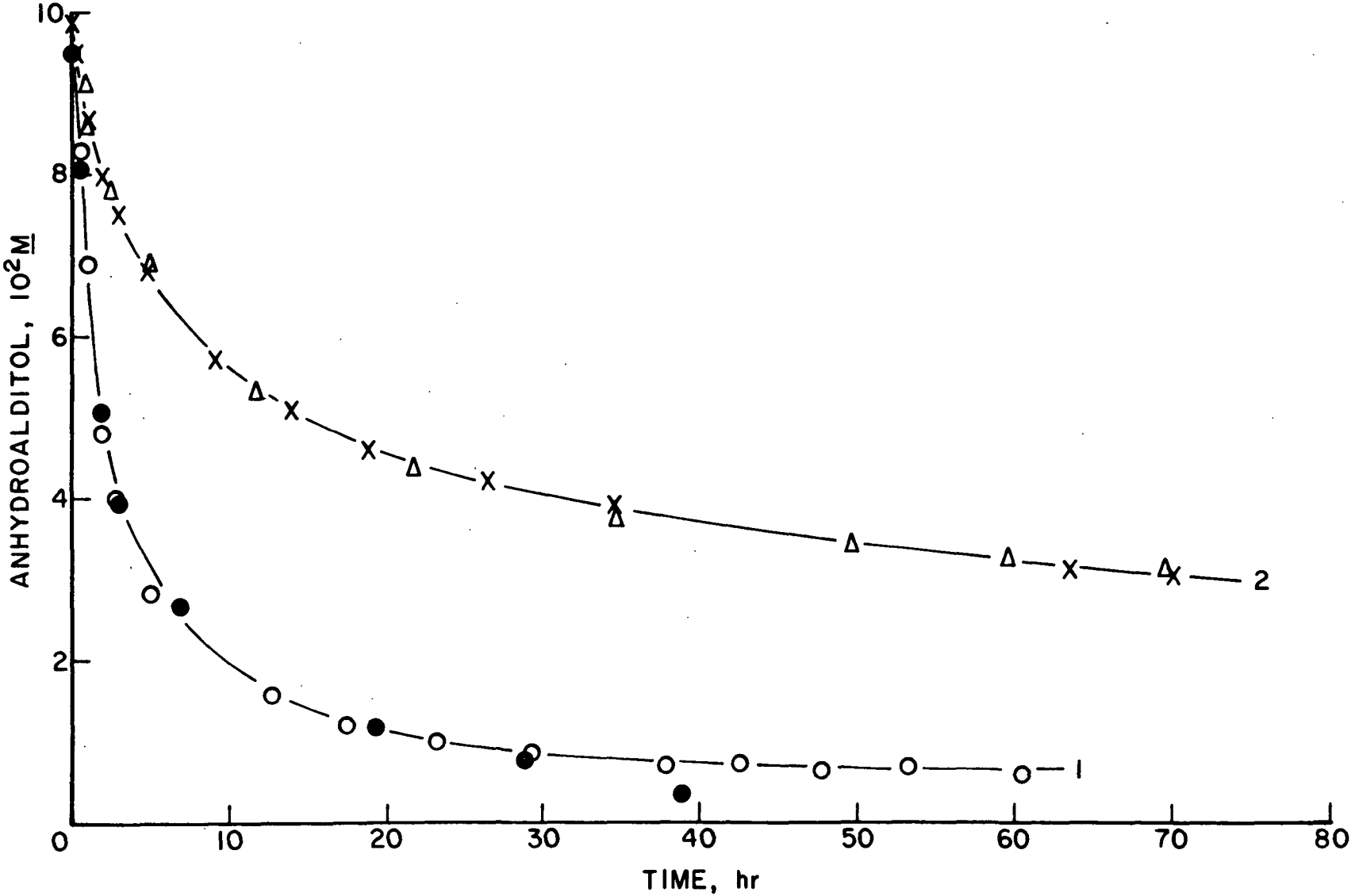


Figure 1. Duplicate Reactions of 0.1M 1,5-Anhydroribitol (1) and 0.1M 1,5-Anhydroxylitol (2) in 1.25N NaOH at 125°C and 75 p.s.i. O_2 (25°C)

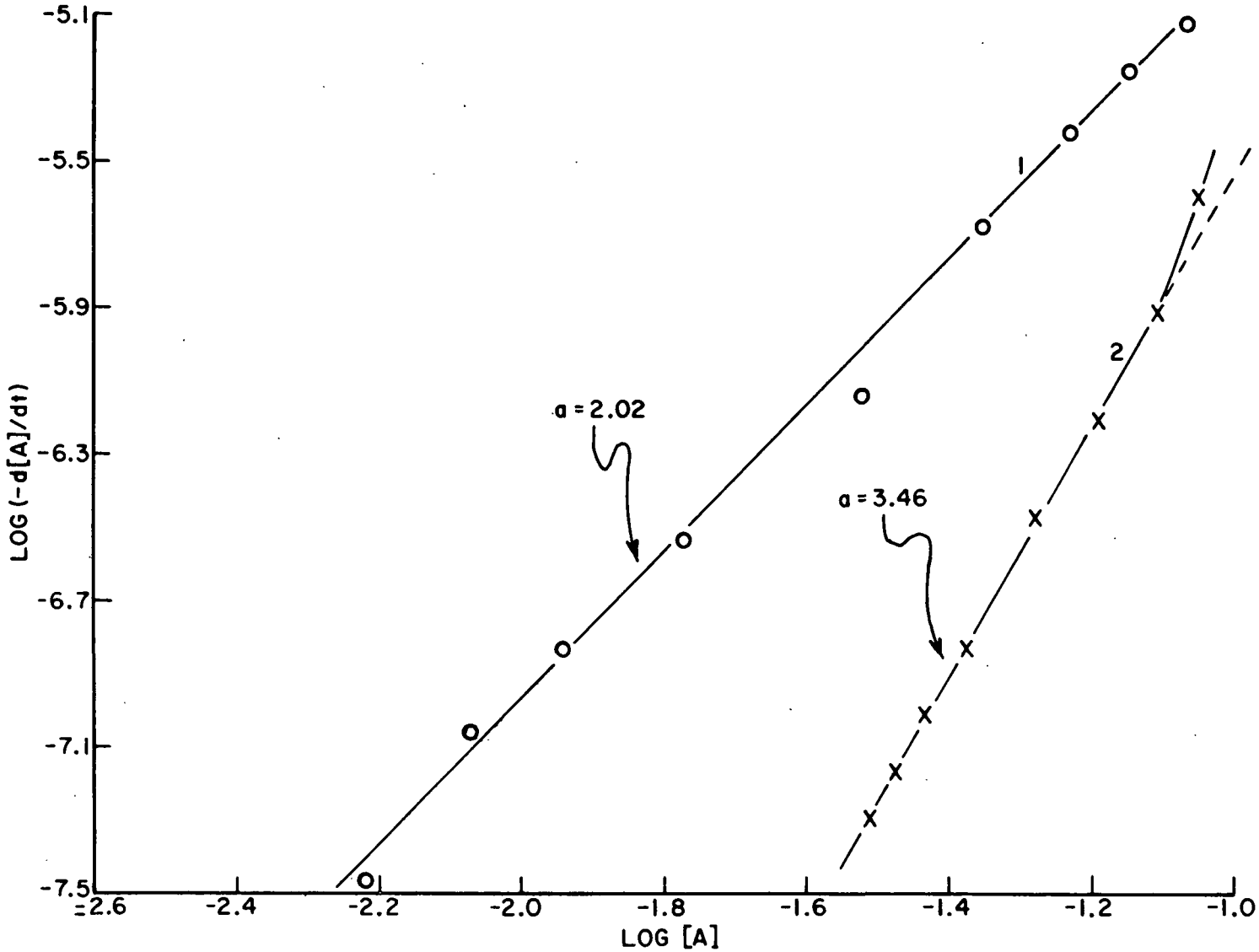


Figure 2. Determination of the Reaction Order, a, with Respect to the Anhydroalditol for 0.1M 1,5-Anhydroribitol (1) and 0.1M 1,5-Anhydroxylitol (2) in 1.25N NaOH at 120°C and 75 p.s.i. O_2 (25°C)

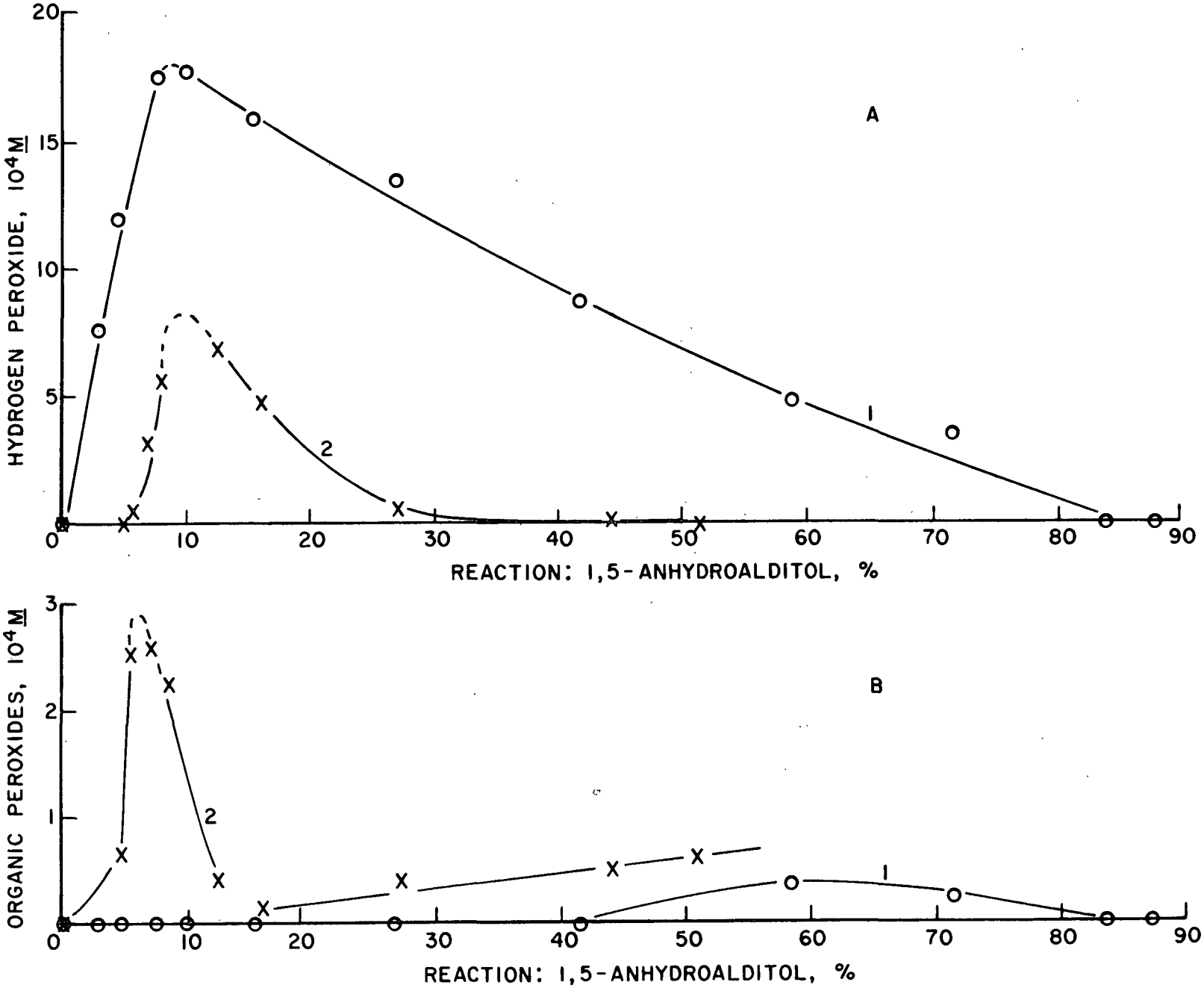


Figure 3. Hydrogen Peroxide (A) and Organic Peroxide (B) Formation in Degradations of 0.1M 1,5-Anhydroribitol (1) and 0.1M 1,5-Anhydroxylitol (2) in 1.25N NaOH at 120°C and 75 p.s.i. O_2 (25°C)

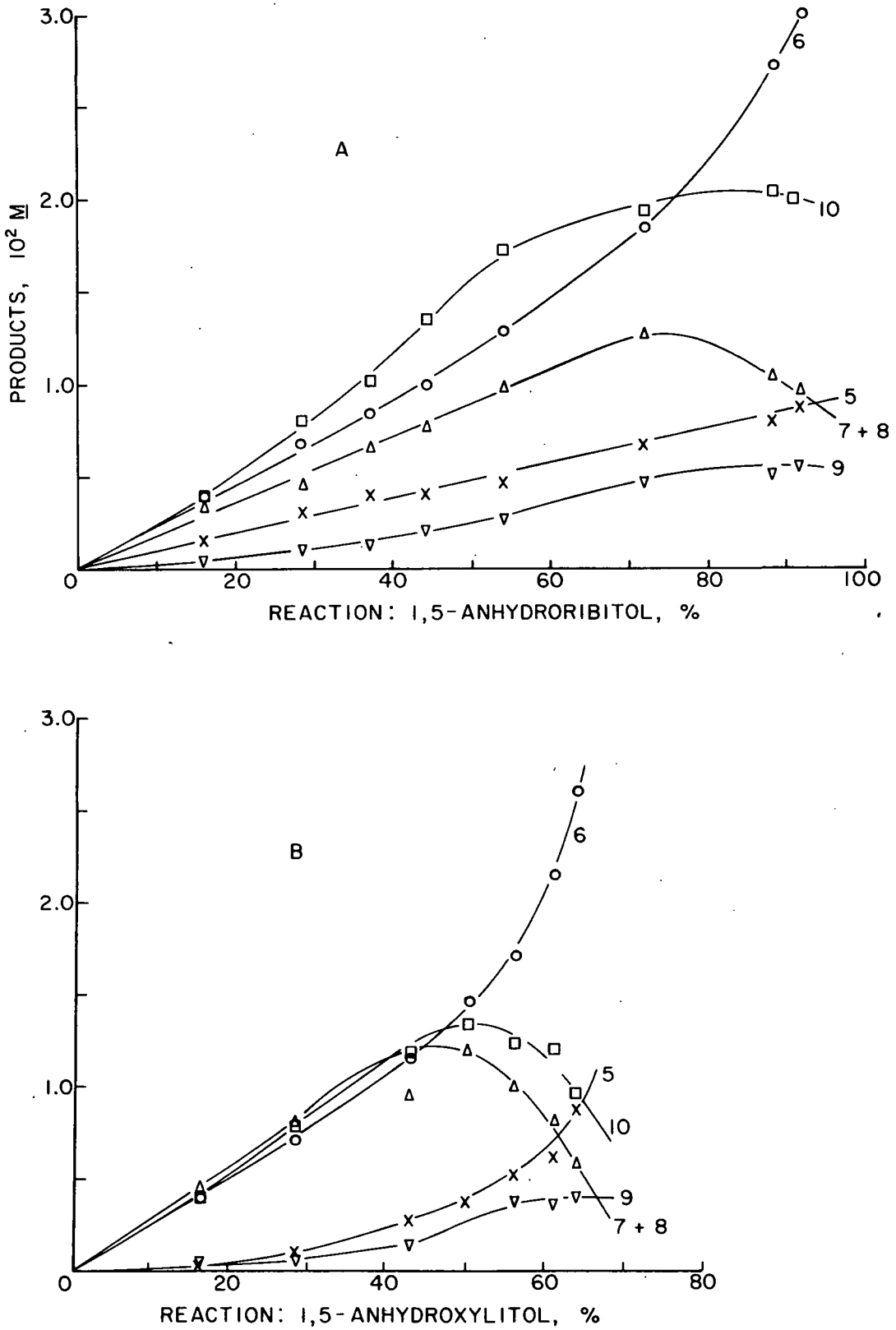
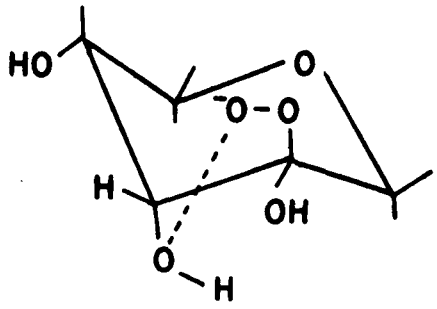
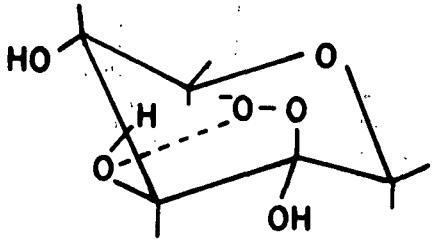


Figure 4. Major Products from Degradations of 1,5-Anhydroribitol (A) and 1,5-Anhydroxylitol (B); lactic acid (5), glycolic acid (6), glyceric acid (7), 2,3-dihydroxybutyric acid (8) 3-O-carboxymethylglyceric acid (9), and 1,4-anhydro-2-C-carboxy-tetritols (10)



O---O ≃ 3.7 Å

AO_2^- (1)



O----O ≃ 2.1 Å

AO_2^- (2)

Figure 5. Minimum Oxygen-oxygen Distances for α-Hydroxyhydroperoxides Formed at C-2 in 1,5-Anhydroribitol (1) and 1,5-Anhydroxylitol (2) in the C_1^4 Conformation. Distances were Determined from Dreiding Molecular Models

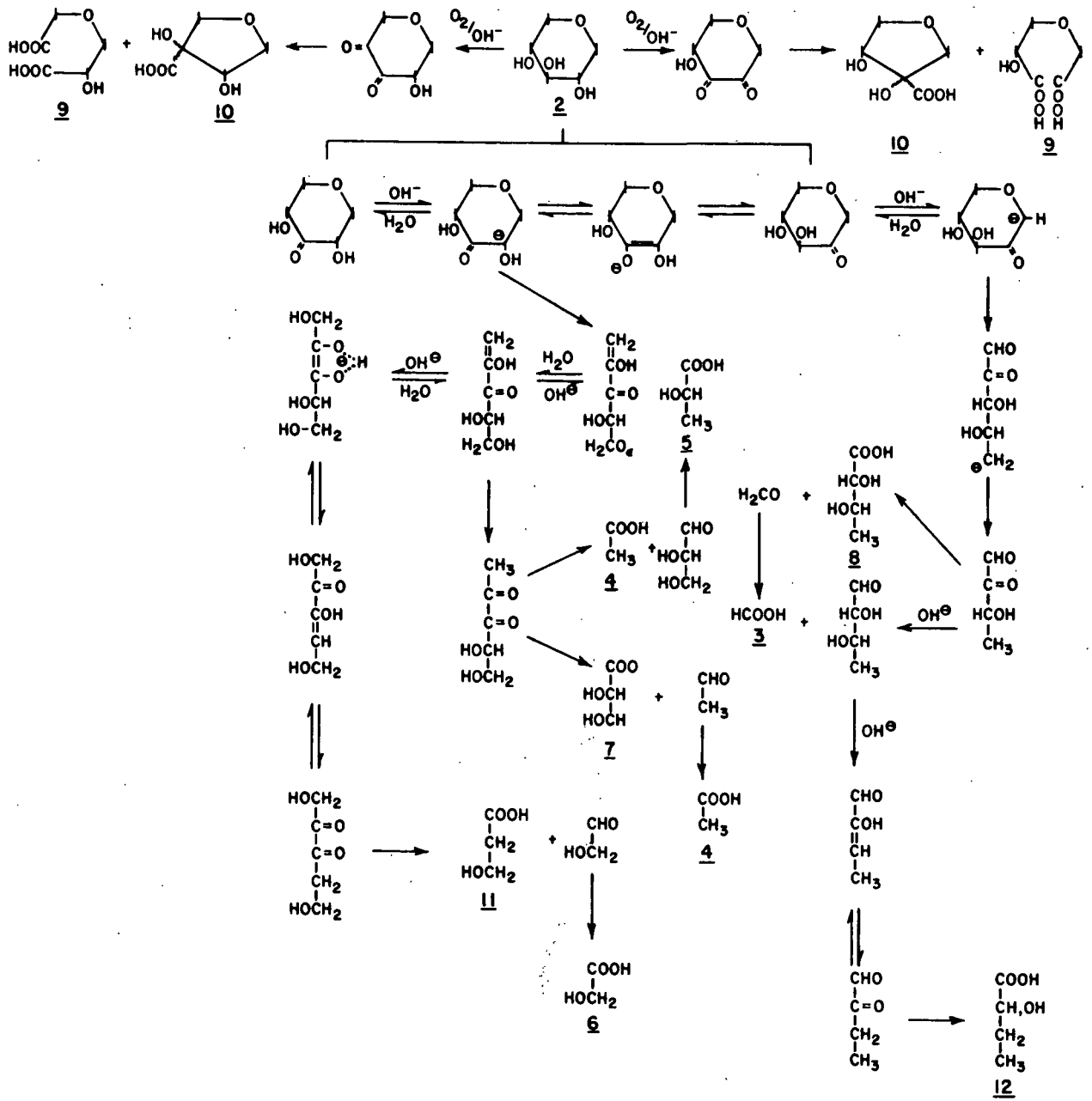


Figure 6. Potential Pathways for Product Formation in Degradations of 1,5-Anhydroalditols (1 and 2)